STUDY OF WINTERIZATION EFFECTS ON CARBON DIOXIDE

WILLIAM N. VANDERPRIOL
T. DE VRIES
PURDUE UNIVERSITY

SEPTEMBER 1953

WRIGHT AIR... DEVELOPMENT CENTER

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

The information furnished herewith is made available for study upon the understanding that the Government's proprietary interests in and relating thereto shall not be impaired. It is desired that the Judge Advocate (WCJ), Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, be promptly notified of any apparent conflict between the Government's proprietary interests and those of others.

FOREWORD

This report was prepared by the Physical Chemistry Department of Purdue University, W. Lafayette, Indiana, under USAF Contract No. AF 33(038)-10959. The research was done under the direction of Dr. Thomas De Vries, Professor of Physical Chemistry, by Wm. N. Vanderkooi, research assistant.

This investigation was performed under Research and Development Order No. 664-800. It was administered under the direction of the Equipment Laboratory, Directorate of Laboratories, Wright Air Development Center, Captain E. C. King acting as project engineer.

ABSTRACT

Phase diagrams of the systems CH_2BrCl-Co_2, CBr_2F -CO_2, and $CBrF_3$-CO_2 were constructed and found to exhibit single eutectics at the low CO_2 content side of the diagrams. The apparatus used to prepare mixtures of known composition is described, as well as the method of cooling which permits visual identification of the freezing points at very low temperatures.

PUBLICATION REVIEW

Manuscript Copy of this report has been reviewed and found satisfactory for publication.

FOR THE COMMANDING GENERAL:

RICHARD STOLLE
Colonel, USAF
Acting Chief, Equipment Laboratory
Directorate of Laboratories

Introduction

The purpose of this research project was to construct the phase diagrams of carbon dioxide and various halogenated methanes. The attainment of the primary purpose necessitated a secondary objective in the development of a suitable method and apparatus for determining the composition of the mixtures as well as their freezing points at very low temperatures. A check of the literature revealed that very little work has been reported on the solubility of CO_2 in organic liquids at low temperatures, and still less on freezing point - composition diagrams of carbondioxide-organic compound systems. This report covers the work done on three such systems: CH_2BrCl-CO_2, CBr_2F_2-CO_2, and $CBrF_3$-CO_2.

Apparatus

Approximately the first half of the period covered by this report was spent in designing, constructing, testing and modifying various types of apparatus before a successful design was found. In general, the apparatus must be able to fulfill two essential requirements. First, there must be some means for either determining the composition of the mixtures or preparing mixtures of known composition. Secondly, it must enable the operator to determine the freezing points of the mixtures accurately.

One of the more promising, but inadequate, methods will be discussed first. The mixing tube consisted of a vacuum jacketed eight inch testtube which was fitted with a three hole rubber stopper. The stopper held an inlet tube with a stopcock about two inches above the stopper, a thermo well, and a short piece of glass tubing to serve as a bearing for a steel wire stirrer. The lower end of the glass stirrer bearing was flanged out slightly and a rubber collar was sealed on the stirrer shaft. The mixing tube could thus be sealed

by drawing the stirrer up until the collar fitted snuggly into the glass flange. The inlet tube was connected with rubber tubing to a 250 ml. gas buret and mercury leveling bulb. The buret, in turn, was connected to a large testtube filled with dry ice and fitted with a two way stopcock by means of which the CO_2 gas could either be admitted to the buret or released into the atmosphere.

To prepare mixtures of known composition the system was first flushed out with CO_2 to remove the air. The stirrer opening was then sealed, as described above, and the mixing tube was placed in liquid nitrogen. Carbon dioxide was admitted in measured quantities from the gas buret into the mixing tube where it solidified. Bromochloromethane was next added through the same inlet tube and stopcock from a 10 ml. buret. The mixing tube was then transfered to a dry ice-acetone bath where it could warm up enough to melt, after which stirring was begun.

To determine the freezing points a seven junction copper-constantan thermopile was used in conjunction with a Leeds and Northrup Micromax recording potentiometer to plot the cooling and warming curves. Liquid nitrogen was used for cooling and the mixtures were permitted to warm up in a dry ice-acetone bath. This method, although promising at first, failed in practice to adequately fulfill either of the two essential requirements. The range of compositions that could be studied was too limited and CO_2 was lost on melting when the mixtures, open to the atmosphere, contained more than about 12 mole percent CO_2. The plotting of cooling curves, although it is a widely used and usually a good method for constructing phase diagrams, did not prove satisfactory in this case. The results were not reproducible and, therefore, unreliable since the changes of slope in the curves at the points where one of the components began freezing out were too slight to be determined accurately.

Profiting from the defects of the unsuccessful methods, a closed glass system was constructed and the freezing points were located visually and the temperatures measured with a potentiometer and thermocouple. This method, although modified slightly for the different compounds, proved successful as is evident from the reproducibility of the data and the wide temperature and composition ranges over which it is applicable.

The apparatus which was used for the CH_2BrCl-CO_2 system will be discussed first and then the modifications which were necessary for the other two systems. The apparatus, see Figure 1, consists essentially of four parts: a manometer, freezing cell, cooling system, and CO_2 and CH_2BrCl measuring equipment.

Pressure and Composition To measure the pressure of the system on eight foot manometer, A, Figure 1, was constructed of large bore capillary tubing. A safety valve in the form of a mercury column, B, was also provided near the lower end of the manometer to prevent excessive pressures building up in the apparatus. In order that the observed pressure may be that of the mixture, the system was evacuated with a mechanical pump before preparing the mixtures. After the apparatus was evacuated to a pressure of 1 mm. Hg or less, stopcock C was turned through 180°, thus disconnecting the pump from the system. The cell, D, was then cooled and CH_2BrCl admitted slowly from the previously filled and weighed weighing tube, E. The CH_2BrCl vaporized readily from the weighing tube and recondensed in the cold cell. The tube was reweighed after enough CH_2BrCl had been transferred to the cell thus giving the weight added by difference, from which the number of moles added was calculated. Carbon dioxide gas, obtained from dry ice, was bubbled through two bottles containing concentrated sulfuric acid, H, and then passed through a twelve inch tube of Drierite. The mercury pressure valve, G, was inserted to permit the CO_2 to escape when stopcock J was closed. To measure the amount

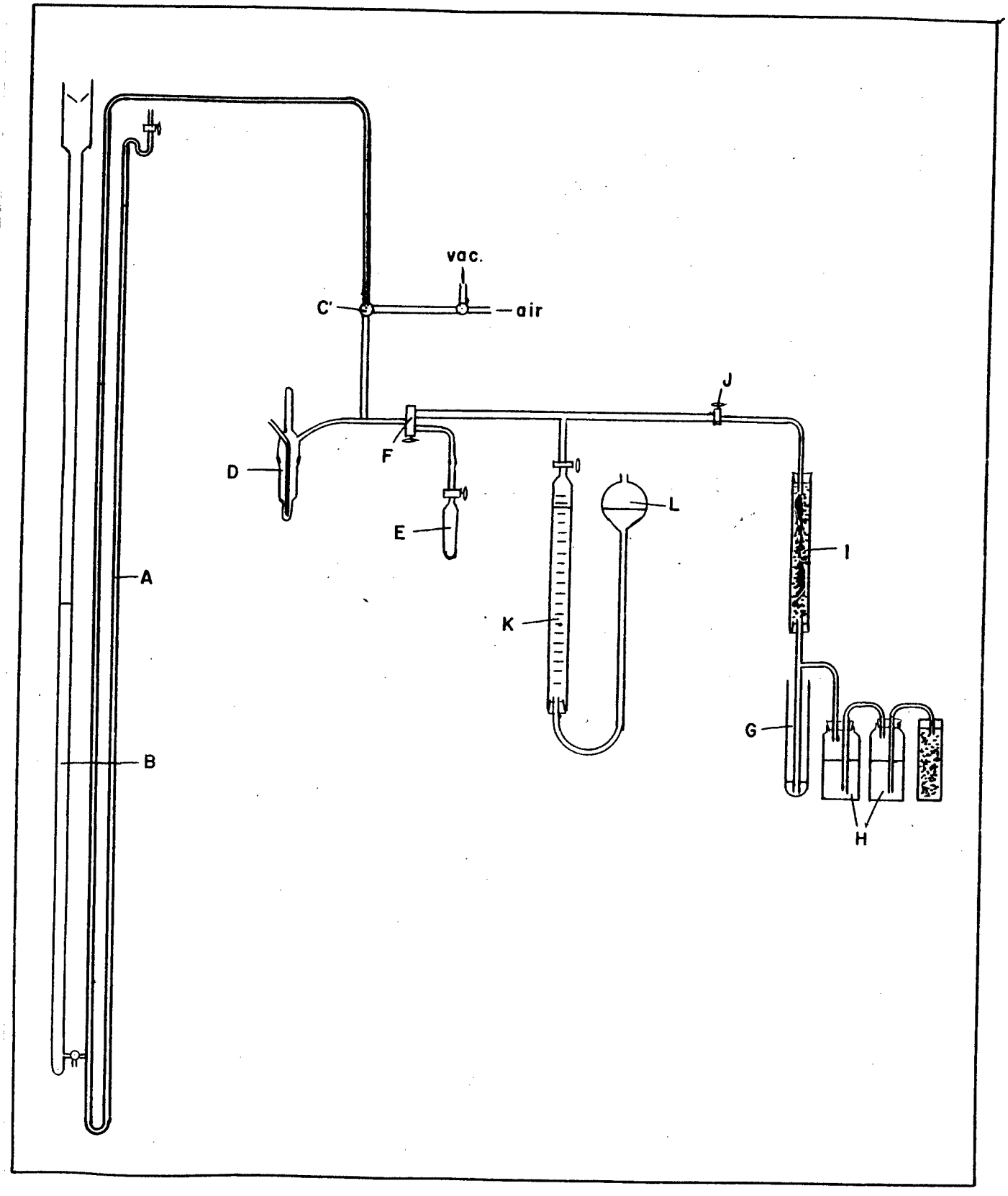

Figure 1

PHASE DIAGRAM APPARATUS

of CO_2 added to the cell stopcock F was closed and J opened until the gas buret, K, was filled with CO_2. The mercury levels in the leveling bulb, L, and in the buret were equalized. Stopcock F was then opened slightly until the desired amount of CO_2 had been admitted to the cell; and the mercury levels were again equalized. The change of mercury level gave the volume of CO_2 added, which, together with the room temperature and atmospheric pressure, gave the number of moles of CO_2 added by using the ideal gas equation, $PV = nRT$. From the number of moles of CH_2BrCl and CO_2 admitted to the cell, the mole percent of CO_2 in the mixture was calculated after making a correction for the amount of CO_2 in the manometer, connecting tubing, and upper part of the cell when the freezing point was reached. No correction was necessary for the CH_2BrCl vapor since its vapor pressure was negligible at the freezing temperature.

For the CBr_2F_2-CO_2 system exactly the same method of preparing the mixtures and calculating their compositions was used as for the CH_2BrCl-CO_2 system. The method had to be revised, however, for the $CBrF_3$-CO_2 system, since $CBrF_3$ is a gas at room temperature. The measuring equipment was, therefore, modified slightly by removing the weighing tube and replacing stopcock J (Fig. 1) with a three way stopcock, so that either $CBrF_3$ from a steel cylinder or CO_2 from the dry ice could be admitted to the buret. Mixtures were prepared by measuring the volumes of both the $CBrF_3$ and the CO_2 which were admitted to and condensed in the cell. The mole percent CO_2 in the mixture was calculated after calculating the number of moles added of each using the ideal gas equation. No correction was applied for the amount of vapor since the vapor pressures of CO_2 and $CBrF_3$ are approximately equal at the freezing temperature and the magnitude of the correction was less than the probable error in the value for the mole percent of CO_2.

Freezing cell. The freezing cell, see Figure 2, is constructed entirely of glass and contains an inlet tube, A, a thermocouple well, B, and a copper wire stirrer, C. The upper end of the stirrer is soldered to a steel bar, D, measuring 1/4 X 1 1/2 inches and is suspended from a light spring, E. The stirrer is alternately raised and lowered with a pair of solenoids, F, which fit around the upper part of the cell. The solenoids are each one inch wide and are wrapped with #24 cotton covered wire to a depth of 1/2 inch. The layers are separated with paper soaked in hot parowax. Direct current of about two amperes is passed alternately through the two coils to give about seventy five stirring cycles per minute. To measure the temperature of the mixture one junction of a thermocouple made from #30 double cotton covered copper wire and #30 double cotton covered constantan wire (1933 calibration) was inserted in the thermo well, and the second junction in a crushed ice bath. The electromotive force of the thermocouple was measured with a Rubicon potentiometer and converted to temperature using the Bureau of Standards publication "Reference Tables for Thermocouples" NBS Circular 508. The value obtained from the tables was corrected according to a calibration curve made by measuring the emf at the freezing point of triply distilled mercury and at the sublimation point of CO_2.

To determine the freezing points of the mixtures, that is, the temperatures at which one of the components begins separating out, the mixtures were cooled slowly and watched while following the temperature drop by keeping the potentiometer balanced. When crystals first appeared in the liquid (many crystals usually appeared suddenly) the emf was read and recorded; and, also, the pressure of the system was read on the manometer immediately. The pressures at the freezing points were thus determined with an accuracy of $\pm$1 cm. Hg. Cooling was then continued until the eutectic temperature was reached. This could easily be identified by the appearance of a different type

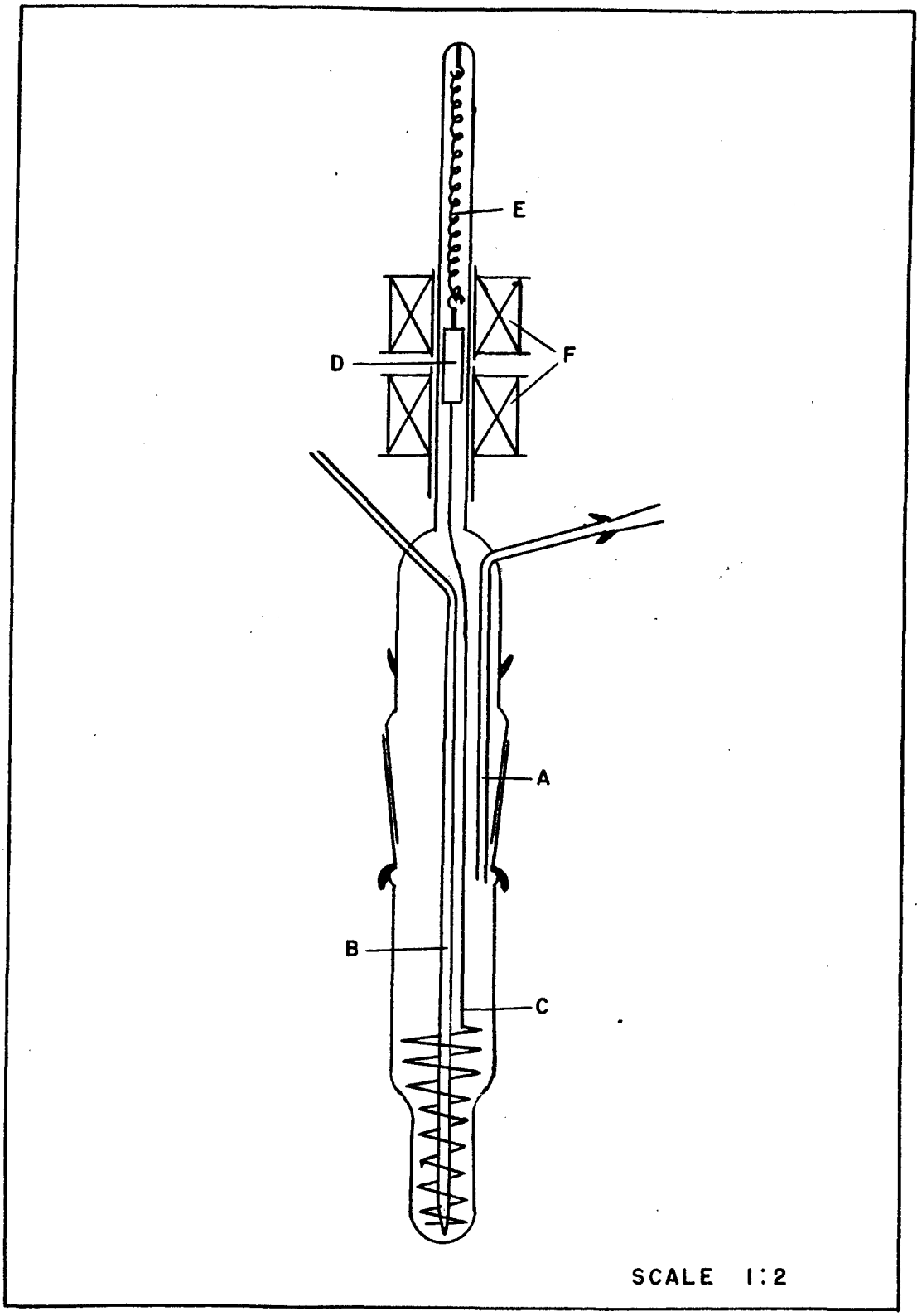

Figure 2

FREEZING POINT CELL

of crystals and by the observation that the temperature assumed a constant value, frequently after rising rapidly a couple degrees when the supercooled liquid froze.

Cooling system. The cooling system, see Figure 3, used for the CH_2BrCl-CO_2 system resulted from a number of unsuccessful, but similar, designs. The freezing cell, A, was partially immersed in a n-propanol bath, B, contained in an unsilvered liter dewar, C. The n-propanol was cooled by passing liquid nitrogen into the coils, D, made from 1/4 inch copper tubing. The liquid nitrogen was transfered from a liter silvered dewar, E, to the coils through a vacuum jacketed and silvered U-tube, F, by applying pressure on the nitrogen surface with a syringe bulb, G. The small amount of ice which accumulated in the liquid nitrogen was filtered out by glass wool in the tube H. A stirrer (not shown) was placed in the n-propanol bath to insure uniform cooling of the bath. With this setup the temperature could be lowered at almost any desired rate or could be maintained constant within a few degrees anywhere between +25° and -120°C by adjusting the rate of addition of liquid nitrogen.

This worked very well for the CH_2BrCl system; but completely failed for the CBr_2F_2-CO_2 and $CBrF_3$-CO_2 systems, since n-propanol freezes at -127°C which is well above the freezing points of CBr_2F_2 and $CBrF_3$. A few other liquids were tried as bath mediums, but none was found that would stay clear at a low enough temperature and still be liquid at room temperature. The method of cooling was, therefore, changed. Liquid nitrogen was used to cool the cell directly instead of using a bath, see Figure 4. An air jacket, A, was placed around the lower end of the cell and a small clear dewar, B, placed around the air jacket to hold the liquid nitrogen which was transfered into it from a silvered dewar as described above. The cell, air jacket, and small dewar were placed in a clear liter dewar, C, with the air jacket and small dewar being supported by a short piece of 3/4 inch rubber tubing, D. Two

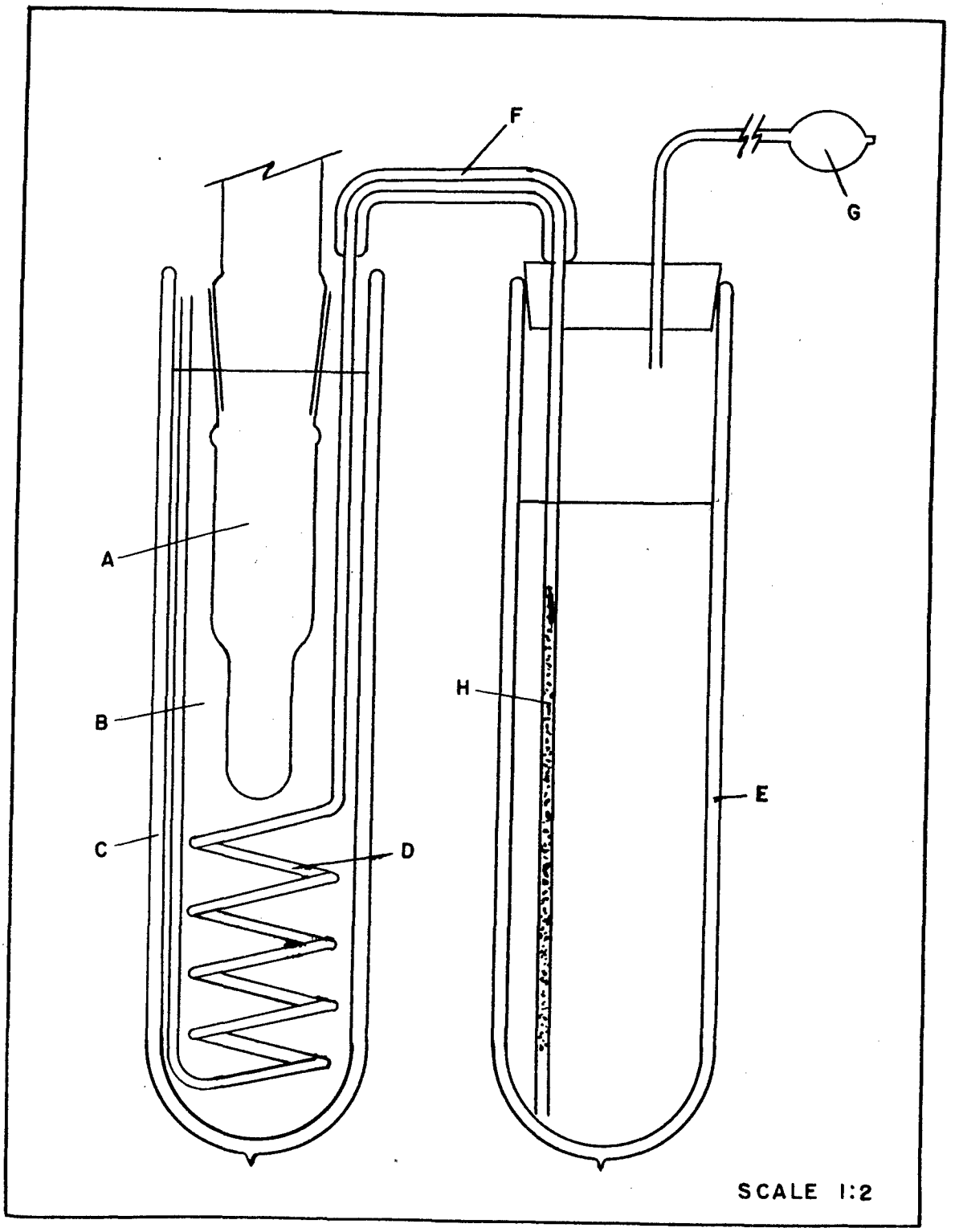

Figure 3

COOLING SYSTEM

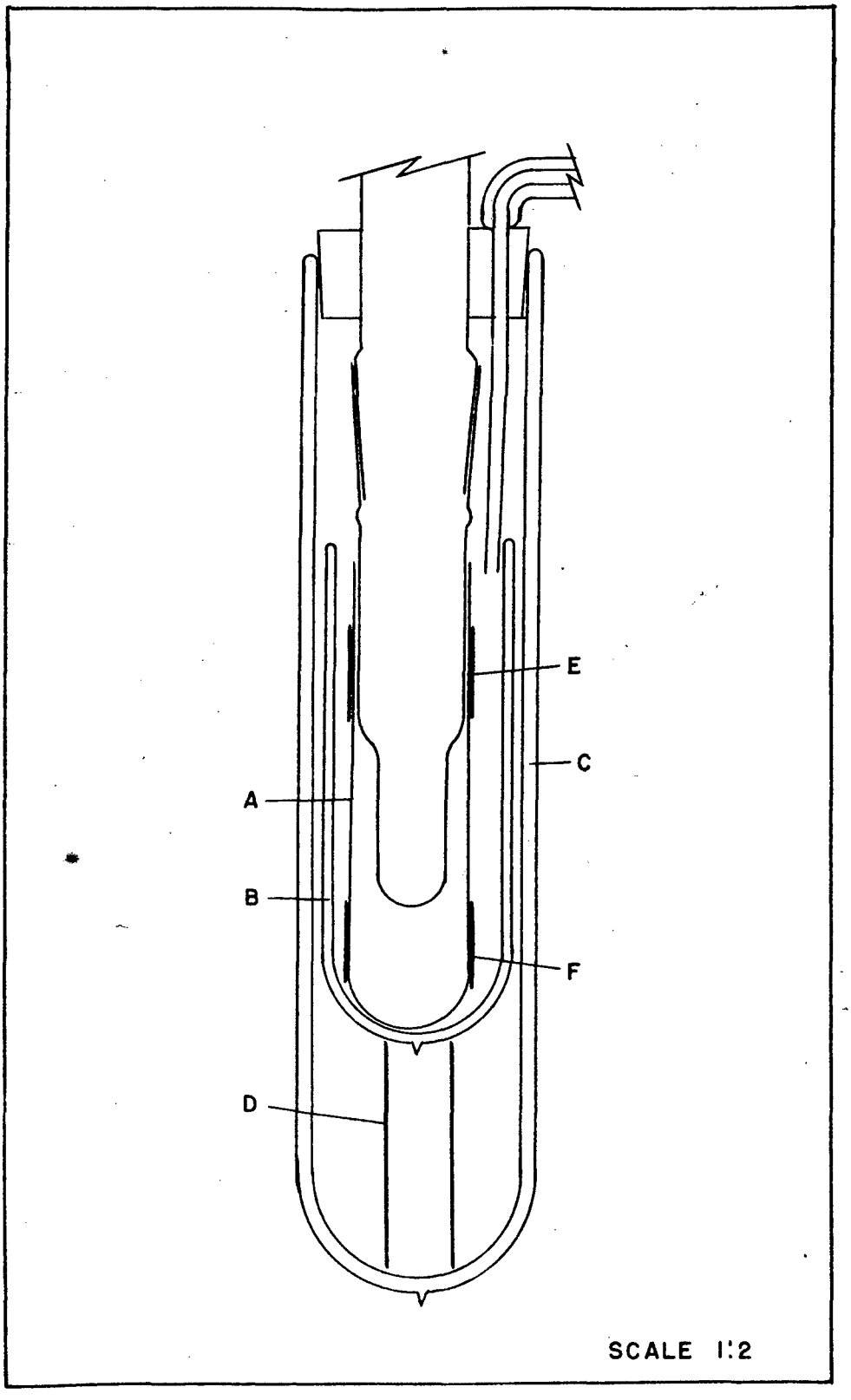

Figure 4

COOLING SYSTEM

heating coils of #22 chromel wire were wrapped around the air jacket and could be heated independently with a current of 1 or 2 amperes. The upper heater, E, was used to prevent the solidification of CO_2 on the sides of the cell above the liquid, and the lower coil, F, to evaporate the excess liquid nitrogen and to warm up the cell after a freezing point had been reached. Without this lower heater it would take a couple hours before the mixtures would melt and before another determination could be made. This method worked very well and was more economical on nitrogen consumption, but reached its limit only slightly below the freezing point of $CBrF_3$. When the temperature of the cell dropped to approximately -170° C, the heat absorbed from the surroundings, mainly through the copper stirrer, equaled the heat absorbed from the cell by the liquid nitrogen; but, since that was cold enough to at least partially freeze the $CBrF_3$, it didn't cause much difficulty.

Results

The phase diagrams of all three systems studied show single eutectic points on the low CO_2 content side of the diagrams. Adding a little CO_2 to the halogenated methanes depressed the freezing points until sufficient has been added to reach the eutected composition. Further addition of CO_2 then caused a very rapid initial rise of the freezing point, but the curve leveled off as compositions of higher CO_2 content were used. Two graphs were constructed for each system studied. The one is the phase diagram in which the freezing point temperature, that is, the temperature at which crystals first appear in the cooling liquid, was plotted against composition expressed in mole percent CO_2. The constant temperature line of the eutectic is also shown on the phase diagrams. The phase diagrams are not constant pressure diagrams, so a second graph was needed to show the variation of the pressure at the freezing points with composition. These two diagrams are, therefore, the projections of a three dimensional curve on planes determined by the temperature and composition axis and the pressure and composition axis, respectively.

In all of the systems studied the pressure of the system just above the freezing points reached the maximum pressure of the manometer and mercury safety valve when the CO_2 content of the mixture was increased to 40 or 50 mole percent CO_2. By the time this composition was reached, though, the curves were no longer greatly curved and could be extrapolated readily to 100% CO_2. This extrapolation is justified since it is unlikely that there will be compound formation or other non-uniformities in the curve.

Baume and Perrot (Baume and Perrot: Journal de Chemie Physique 12, 225 (1914)) determined the phase diagrams of the systems CH_3OH-CO_2 and CH_3OCH_3-CO_2. Both of these had a single eutectic of low CO_2 content and can reasonably be expected to be similar to the diagrams of the systems reported here.

The $CBrF_3$-CO_2 system has a eutectic mixture containing less than 0.5 mole percent CO_2 and freezing at approximately -170°C. Due to the experimental difficulties in cooling to such a low temperature and to the impure nature of the $CBrF_3$, the eutectic temperature of the mixtures and the freezing point of $CBrF_3$ could not be determined with any great degree of accuracy. The freezing points of the mixtures, however, were determined with an accuracy of $\pm$ 0.4°C.

The $CBrF_3$ as it was obtained from a steel cylinder was far from pure. It contained an impurity of 9.5% CO_2. (The amount of impurity was determined using the completed phase diagram and the freezing point of the unpurified material). The CO_2 was removed by passing the gas through a tube filled with Ascarite. This treatment removed all the CO_2 but the $CBrF_3$ still contained some impurity. When the CO_2-free $CBrF_3$ was cooled crystals appeared at -167°C., but the liquid froze very slowly and the temperature fluctuated over a couple degree range during the freezing. The value given in Table 1 (-168°)is the average of ten values for the freezing point of $CBrF_3$.

The data for the $CBrF_3$ - CO_2 system is tabulated in Table 1 and represented graphically in Figures 5 and 6. On the phase diagram (Fig. 5) the curve beginning at the lower left hand corner and extending to the upper right represents the freezing points of the mixture. The other curve represents the boiling points of the mixture being the 760 mm isobar.

Table 1

Data for Phase Diagram of $CBrF_3$-CO_2

Composition (CO_2)	Freezing Point (°C)	Eutectic (°C)	Pressure (cm. Hg)	Boiling Point (°C)
0	-168		5	-64.7
0.8	-154.2		4.5	
1.1	-150.9		2.4	
2.0	-137.0			
2.4	-136.1		6.0	
4.9	-121.8		8.4	
10.0	-107.6		21.0	-74.7
10.2	-108.1		15.8	-72.4
15.1	-102.1		27.9	-77.9
15.1		-170.4	6.0	
15.5	- 99.5		30.9	
19.5	- 95.0		53.4	
20.6	- 94.9		39.1	-80.5
22.2	- 92.7		49.2	-81.7
28.4	- 89.0		54.2	
33.8	- 83.7		79.0	-84.1
37.2	- 82.4		98.7	
38.3	- 81.7		81.0	-84.5
46.7	- 76.9		121.7	
50.0*	- 75.5		143	-84.6
60.0*	- 71.0		187	-84.0
70.0*	- 66.7		234	-83.1
80.0*	- 62.9		285	-81.7
90.0*	- 59.5		337	-80.2
100.0º	- 56.6		388.5	-78.5

* Estimated from extrapolated graph

º Values obtained from "Int.Crt. Tables" 3, 235 (1928)

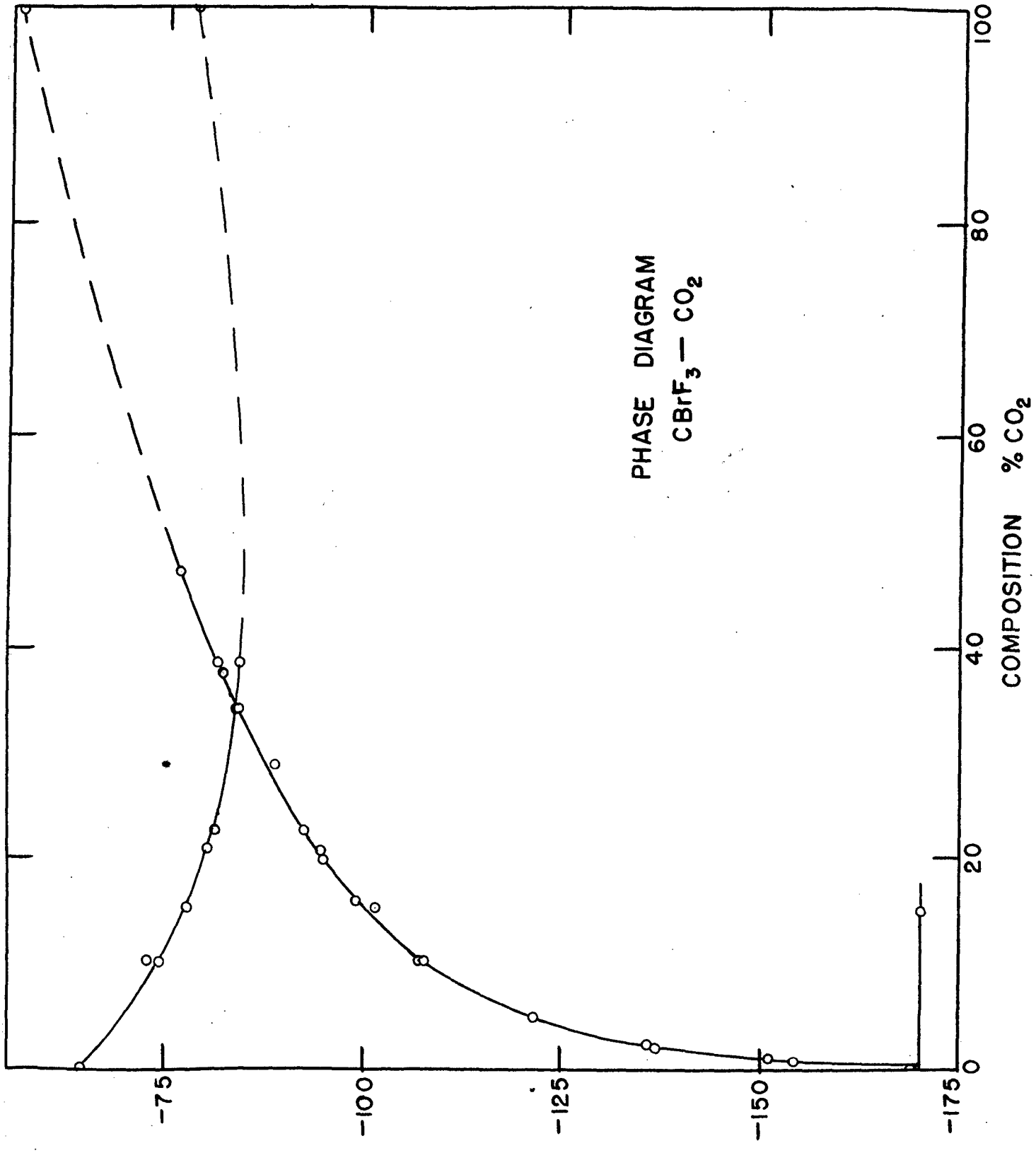
PHASE DIAGRAM
$CBrF_3 - CO_2$
COMPOSITION % CO_2
0
20
40
60
80
100
-75
-100
-125
-150
-175
TEMPERATURE (°C)

Figure 5

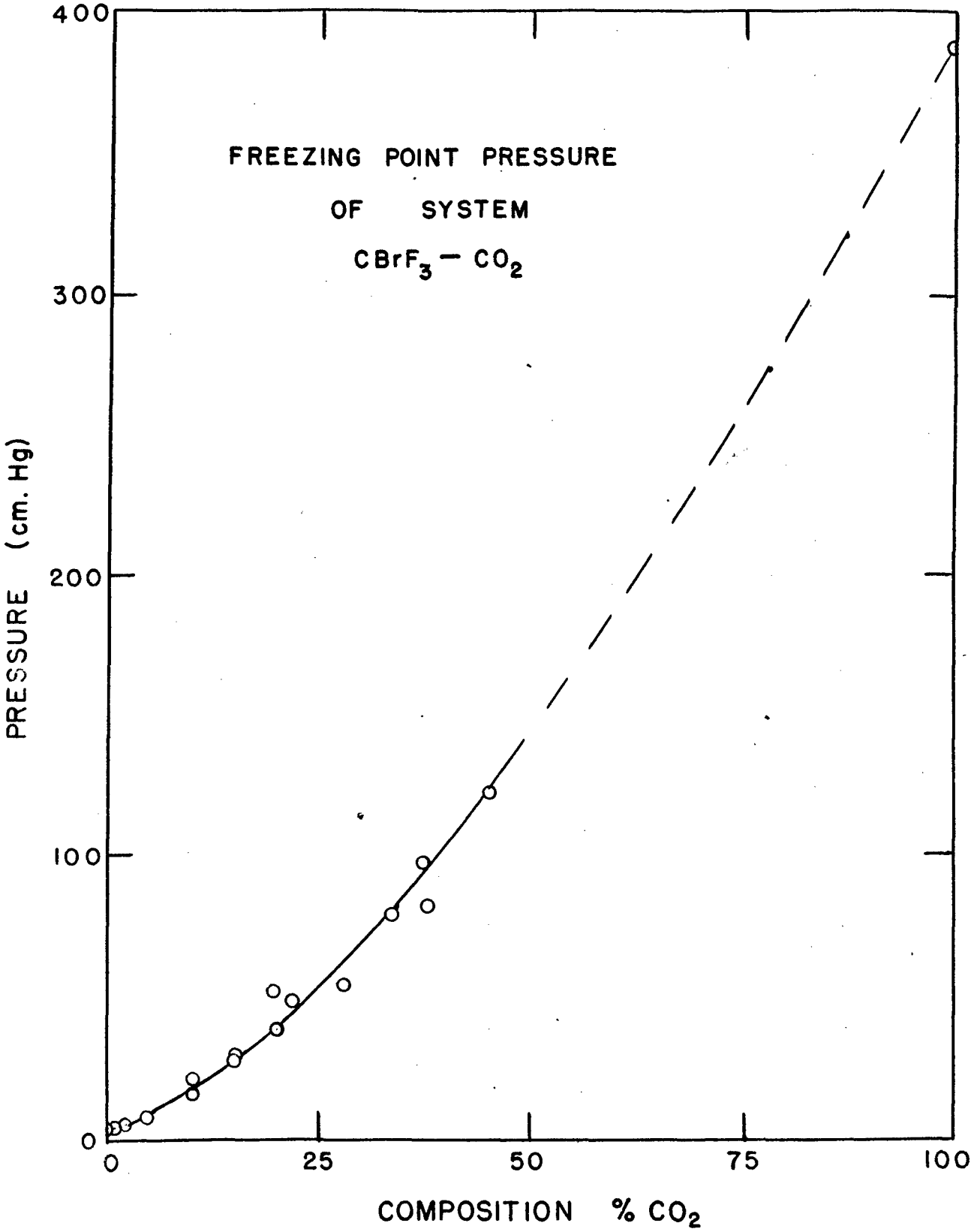
FREEZING POINT PRESSURE
OF SYSTEM
$CBrF_3 - CO_2$
PRESSURE (cm. Hg)
400
300
200
100
0
0
25
50
75
100
COMPOSITION % CO_2

Figure 6

The CBr_2F_2-CO_2 system has a single eutectic at -142.6 ± 0.1°C and a eutectic composition of 0.5 mole percent CO_2. CBr_2F_3 was pure as it was obtained from the shipping cylinder. It freezes at -141.6°C.

Table 2

Data for the Phase Diagram of CBr_2F_2-CO_2

Composition (% CO_2)	Freezing Point (°C)	Eutectic (°C)	Pressure (cm. Hg.)
0	-141.6		0.5
0.4	-141.6		0.4
0.7	-141.4	-142.5	0.4
1.3	-133.4		0.8
2.3	-127.7	-142.7	0.4
3.6	-120.2		1.5
5.0	-114.8	-142.7	2.8
9.7	-104.0		11.4
12.9	- 99.0		14.4
16.2	- 93.2		27.7
18.5	- 88.8		
20.1	- 88.2		38.1
28.2	- 80.7		78.9
35.9	- 77.5		91.8
36.8	- 76.3		97.4
41.7	- 74.6	-142.6	111.0
47.2	- 71.7		145.0
60.0*	- 67.3		193.
70.0*	- 64.2		239
80.0*	- 61.4		289
90.0*	- 58.9		338
100.0♣	- 56.6		388.5

* Values are estimated from the extrapolated graph.

♣ Values obtained from "Int. Crit. Tables" 3, 235 (1928).

The freezing points of the mixtures were obtained with an accuracy of ± 0.4°C and are given together with the pressures at the freezing points, the compositions and eutectic temperature in Table 2 and are represented graphically in Figures 7 and 8.

The CH_2ClBr-CO_2 system differed from the other two in that the eutectic came at a much higher CO_2 content. The system has a single eutectic at 11.2 mole percent CO_2 and a eutectic temperature of -92.1°C. Both the freezing points and the eutectic temperature were determined with an accuracy

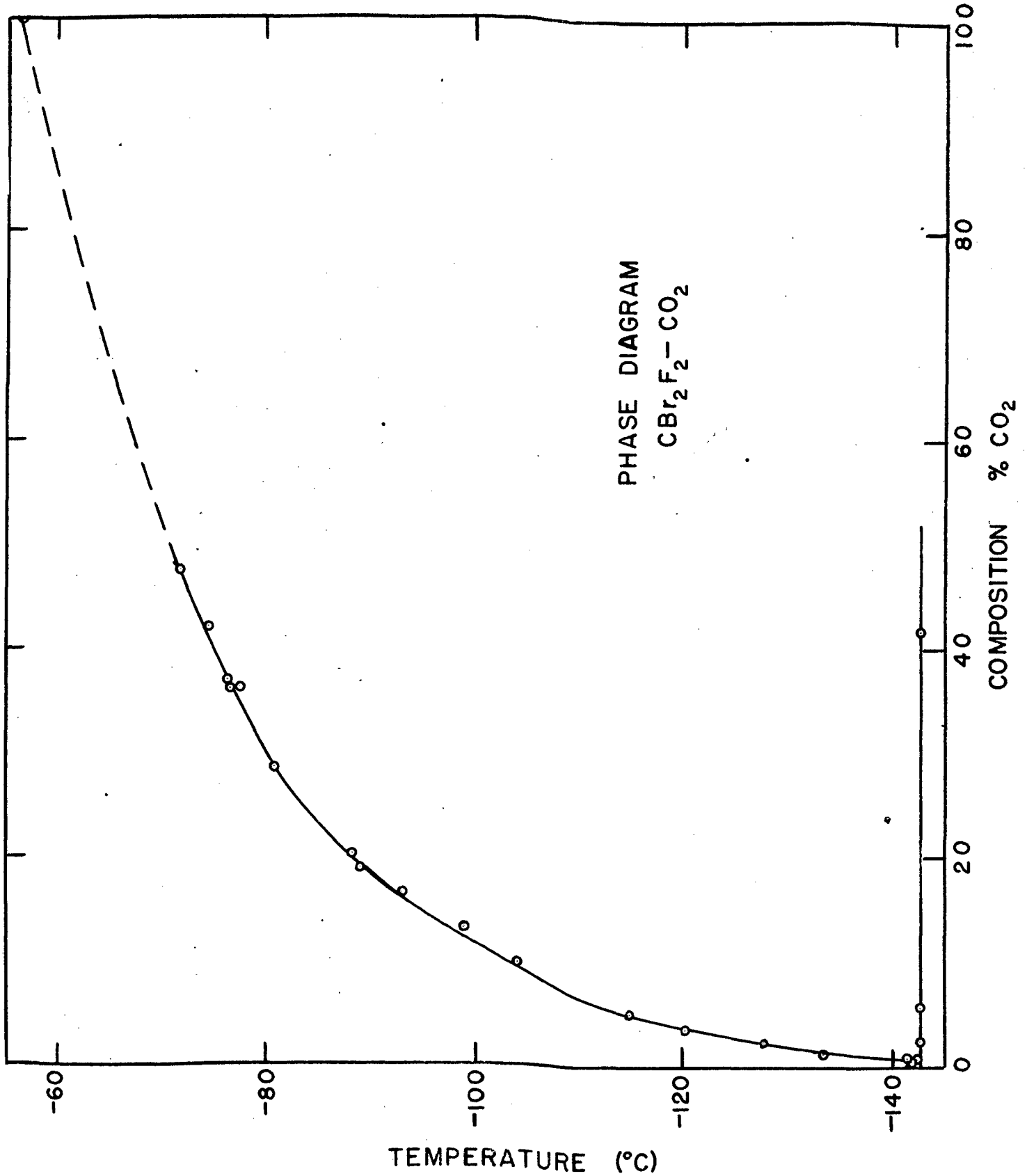
PHASE DIAGRAM
$CBr_2F_2 - CO_2$
COMPOSITION % CO_2
0
20
40
60
80
100
-60
-80
-100
-120
-140
TEMPERATURE (°C)

Figure 7

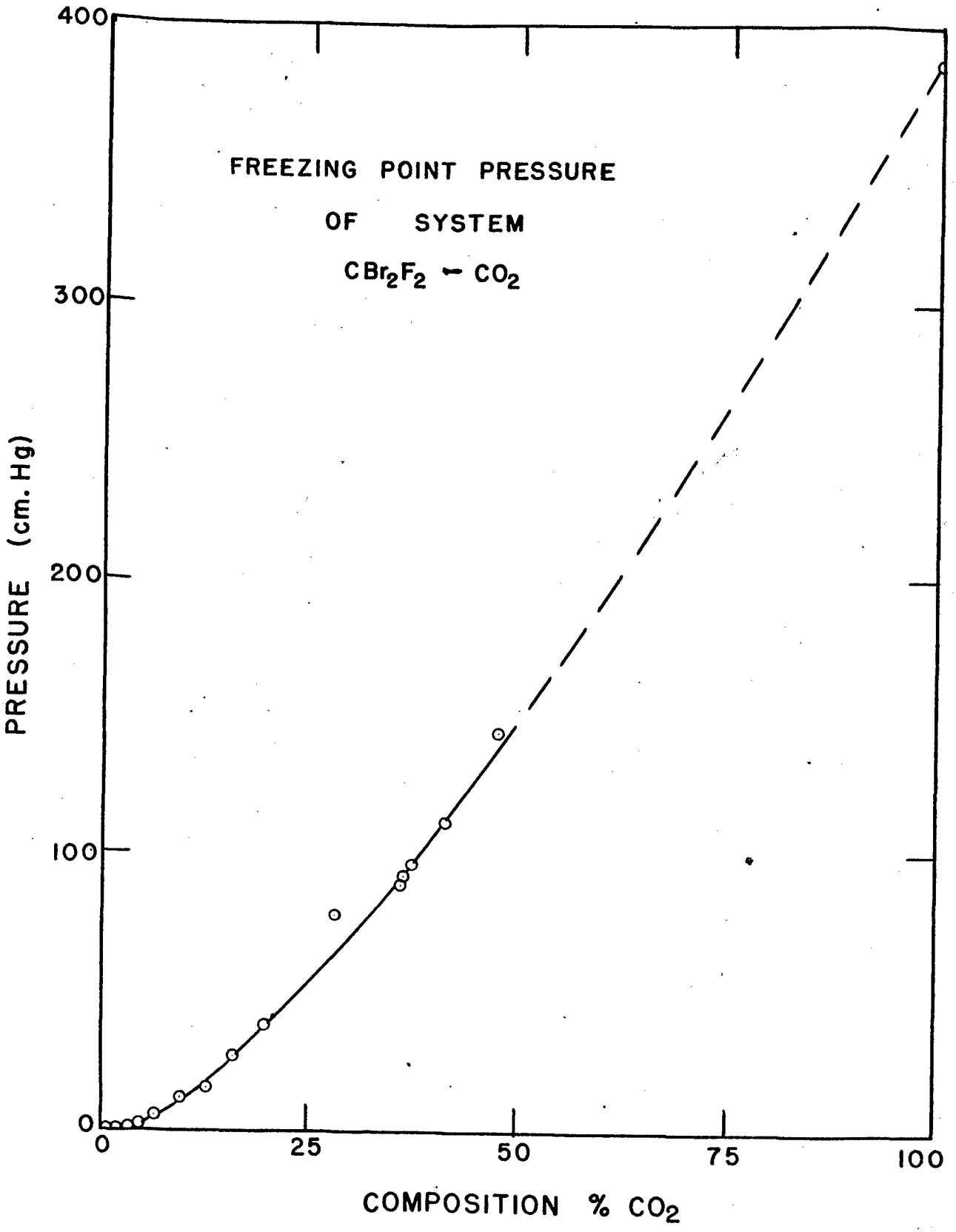
FREEZING POINT PRESSURE
OF SYSTEM
$CBr_2F_2 - CO_2$
PRESSURE (cm. Hg)
400
300
200
100
0
0
25
50
75
100
COMPOSITION % CO_2

Figure 8

of ± 0.1°C. The composition of the mixtures, the freezing points, eutectics, and system pressure at the freezing points are given in Table 3 and Figures 9 and 10.

Table 3

Data for the Phase Diagram of CH_2BrCl-CO_2

Composition (% CO_2)	Freezing Point (°C)	Eutectic (°C)	Pressure (cm. Hg)
0	-87.9	----	0.2
4.0	-89.8	----	14.7
4.6	-89.9	----	14.8
6.0	-90.5	----	19.8
8.4	-91.3	----	21.9
10.6	-92.9	-92.1	23.6
11.7	-91.7	-92.1	28.7
12.1	-90.4	-92.1	31.1
15.8	-85.5	-92.1	48.0
17.4	-84.5	-92.1	54.8
21.6	-80.0	----	79.3
25.6	-76.6	----	100.1
29.2	-73.8	----	122.6
32.6	-72.0	----	137.3
35.8	-70.8	----	149.1
38.8	-69.7	-92.1	160.7
40.0*	-69.4	----	166
50.0*	-66.4	----	205
60.0*	-64.2	----	242
70.0*	-62.2	----	280
80.0*	-60.3	----	316
90.0*	-58.3	----	352
100.0≠	-56.6	----	388.5

* Values are estimated from the extrapolated graph.

≠ Value obtained from "Int. Crit. Tables" 3, 235 (1928).

The CH_2BrCl was purified by fractionation before use. The middle fraction was collected for use and had a constant boiling point of 67°C at 750 mm. and a freezing point of -87.9°C.

Mixtures containing less than 11.2 mole percent CO_2 exhibited super cooling of as much as two or three degrees before crystals appeared and the temperature jumped up to the freezing point of the mixture. In this connection it is interesting to note in Fig. 9 that a point was obtained below

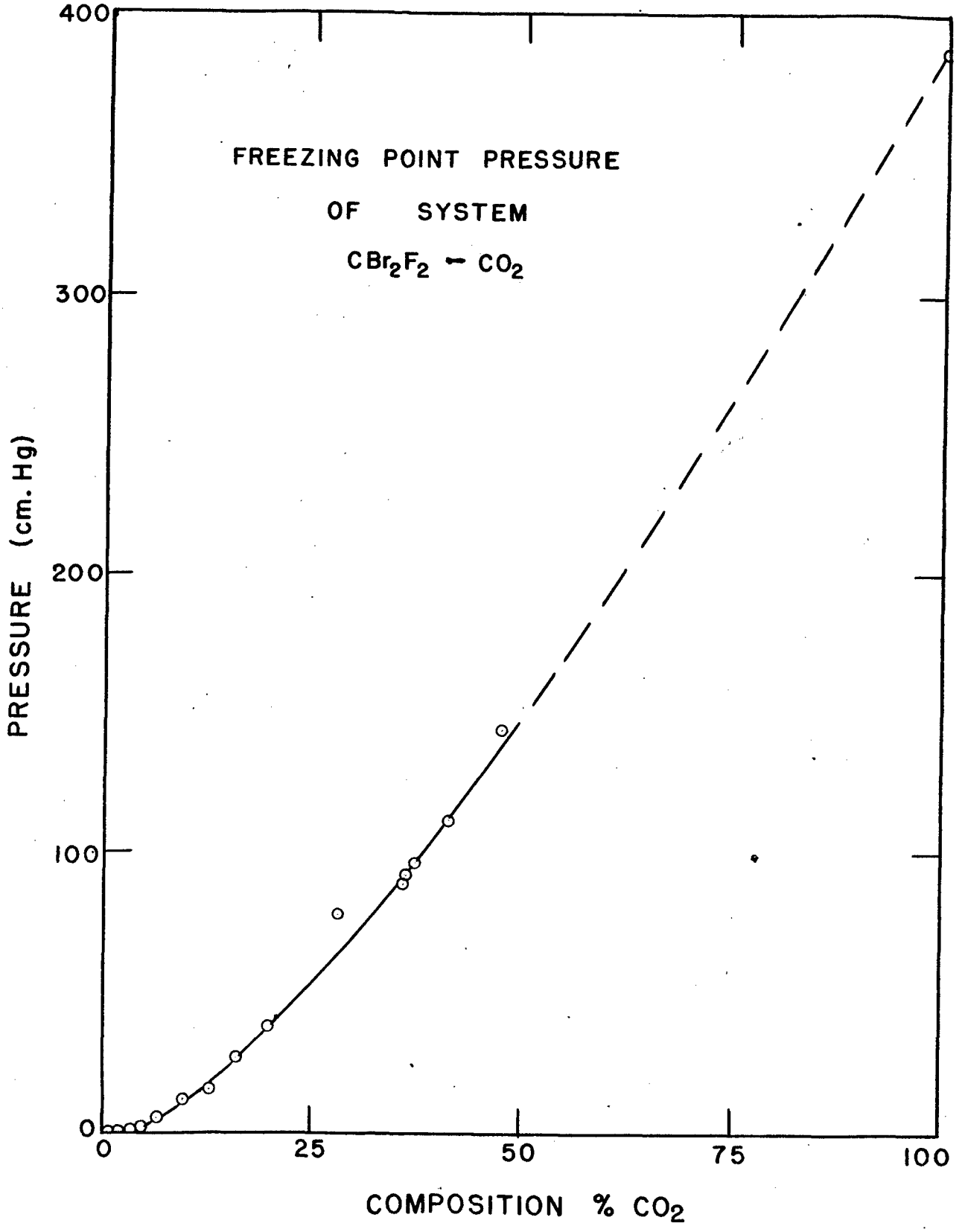
FREEZING POINT PRESSURE
OF SYSTEM
CBr_2F_2 – CO_2
PRESSURE (cm. Hg)
400
300
200
100
0
0
25
50
75
100
COMPOSITION % CO_2

Figure 8

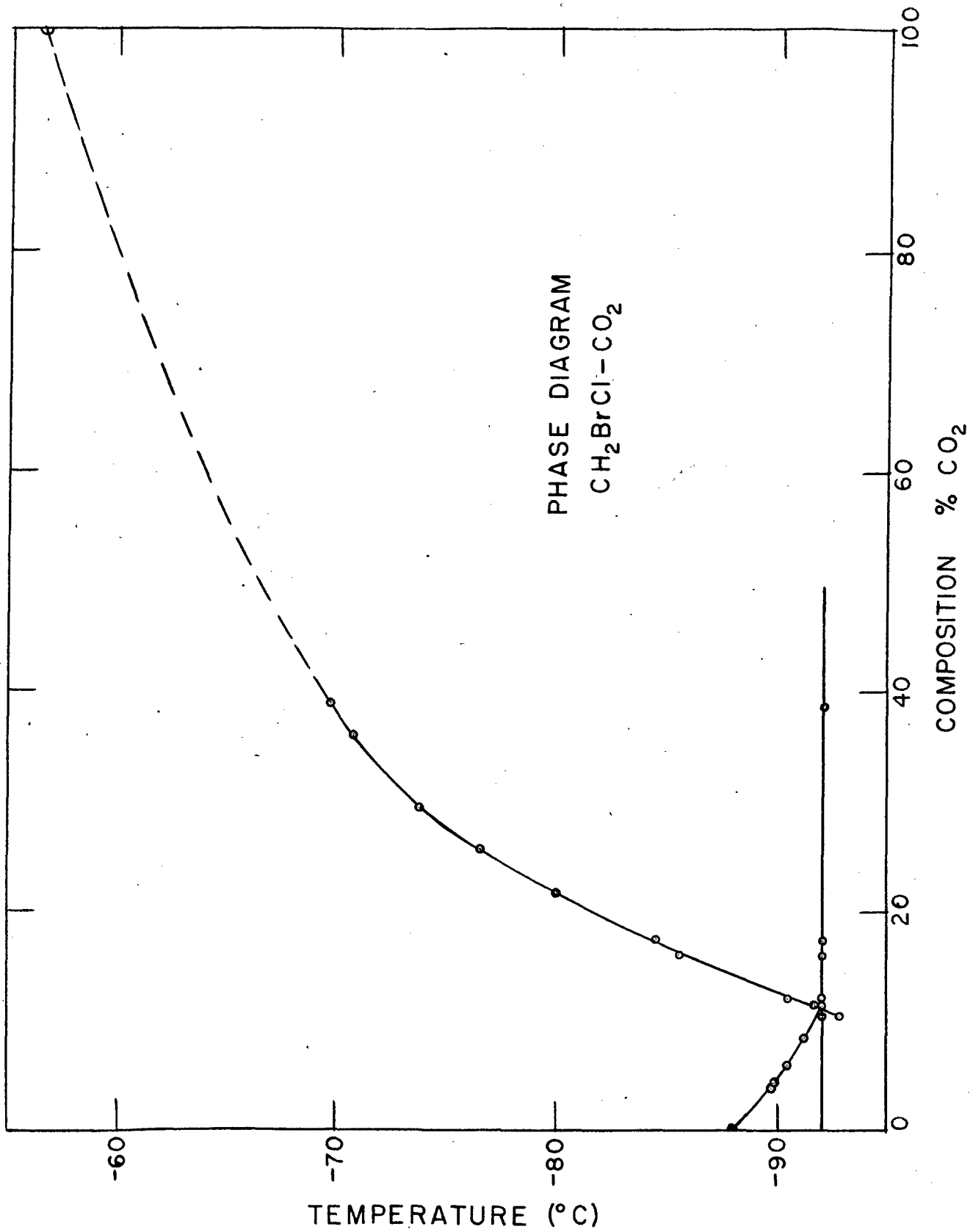
PHASE DIAGRAM
$CH_2BrCl - CO_2$
COMPOSITION % CO_2
0
20
40
60
80
100
-60
-70
-80
-90
TEMPERATURE (°C)

Figure 9

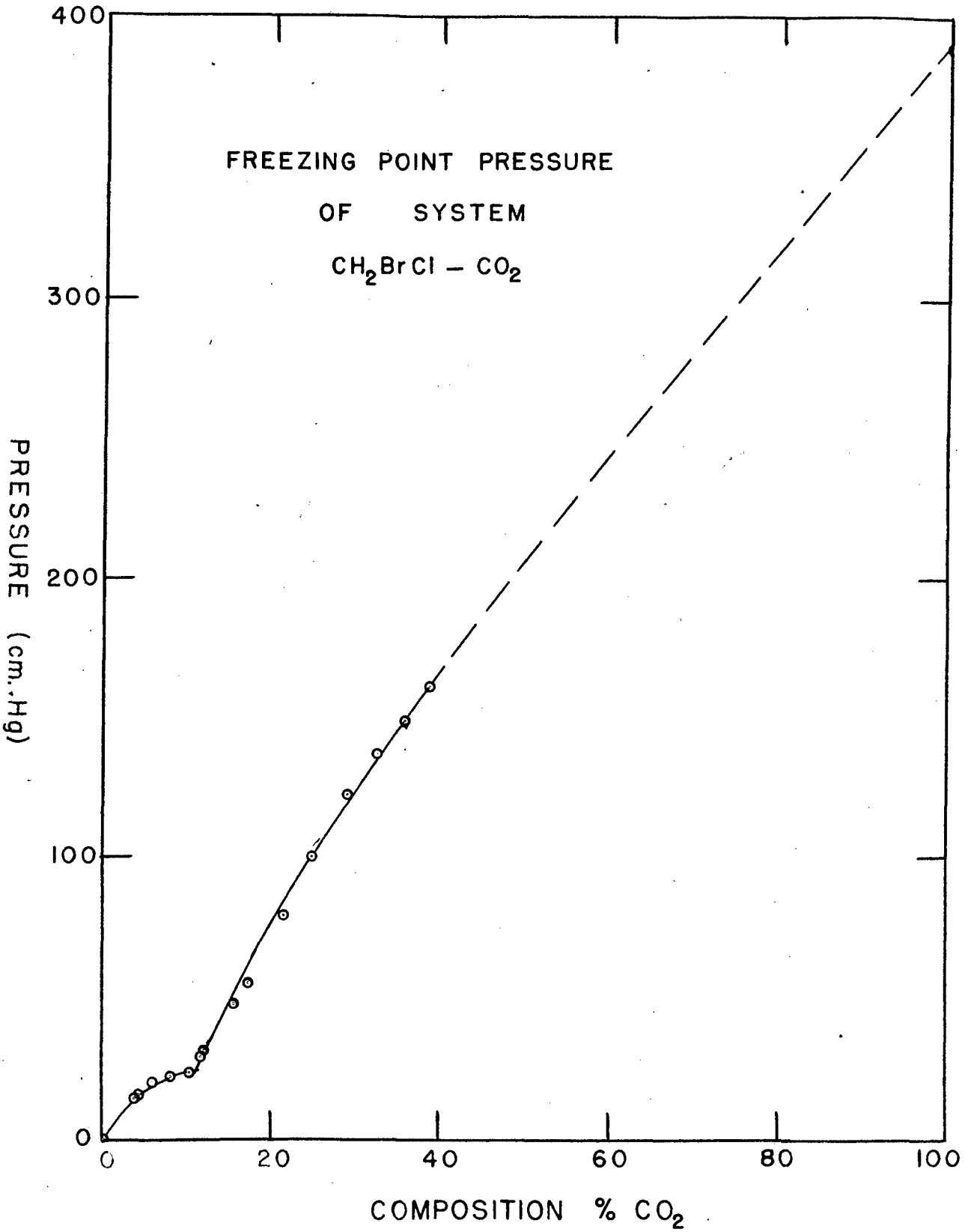
FREEZING POINT PRESSURE
OF SYSTEM
$CH_2BrCl - CO_2$
PRESSURE (cm. Hg)
400
300
200
100
0
0
20
40
60
80
100
COMPOSITION % CO_2

Figure 10

the eutectic temperature and on the freezing-point line of mixtures of higher CO_2 content. This was obtained in a super cooled liquid and, being in a metastable state, the temperature jumped up to the eutectic temperature when the entire mixture froze.

An unrelated, but possibly significant behavior of two of these compounds, was noticed while working with CBr_2F_2. Both CBr_2F_2 and $CBrF_3$ decompose at high temperatures liberating free bromine. It was observed while repairing a crack in the glass tubing of the apparatus, while there was still CBr_2F_2 vapor in it, that a reaction took place inside the heated soft section of the Pyrex tubing. By the time the crack was repaired the tubing was filled with brown vapor and there was a distinct odor of Br_2.

This is mentioned here since it would be a very undesirable property from a health stand point if these compounds are to be used where they may be heated to high temperatures.